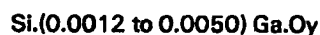
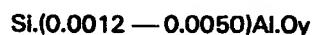


# (12) UK Patent Application (19) GB (11) 2 023 562 A

(21) Application No 7921621  
(22) Date of filing 21 Jun 1979  
(23) Claims filed 21 Jun 1979  
(30) Priority data  
(31) 24843  
30884  
22639  
(32) 22 Jun 1978  
15 Dec 1978  
14 May 1979  
(33) Italy (IT)  
(43) Application published  
3 Jan 1980  
(51) INT CL<sup>3</sup>  
C01B 33/12 33/28 C01G  
17/02  
(52) Domestic classification  
C1A 13 410 411 423 425  
519 CE D31 D41 DX G12  
G12D41 G12DX G1 G4  
G50 G55 N4 N54 N55 VG1  
(56) Documents cited  
GB 1261616  
GB 1246852  
GB 807272  
(58) Field of search  
C1A  
(71) Applicants  
Snamprogetti S.p.A.,  
Corso Venezia 16, Milan,  
Italy  
(72) Inventors  
Marco Tarasimasso, Orfeo  
Forlani, Giovanni Manara,  
Bruno Notari  
(74) Agents  
Haseltine Lake & Co

## (54) Modified silica and germania

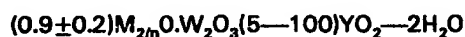
(57) Aluminium- or gallium modified silica or germania is prepared by reacting an aluminium (or gallium) derivative and a silicon (or germanium) derivative with a clathrating substance with the possible addition of a mineralising agent and an inorganic base, and crystallising the mixture thus obtained, so that a compound is formed which has the general formula:



in which y is from 2.0018 to 2.0075.

The modified silicas and the analogous compounds are efficient catalysts for a large number of reactions.

A zeolite of formula



in which M is  $\text{H}^+$ ,  $\text{NH}_4^+$ , metallic cations or cations derived from amino alcohols, W is Al or Ga, Y is Si or Ge and z is 0-40 of ZSM-5 type is referred to as a modification.

The drawings originally filed were informal and the print here reproduced is taken from a later filed formal copy.

GB 2 023 562 A

2023562

1/2

**Fig.1**

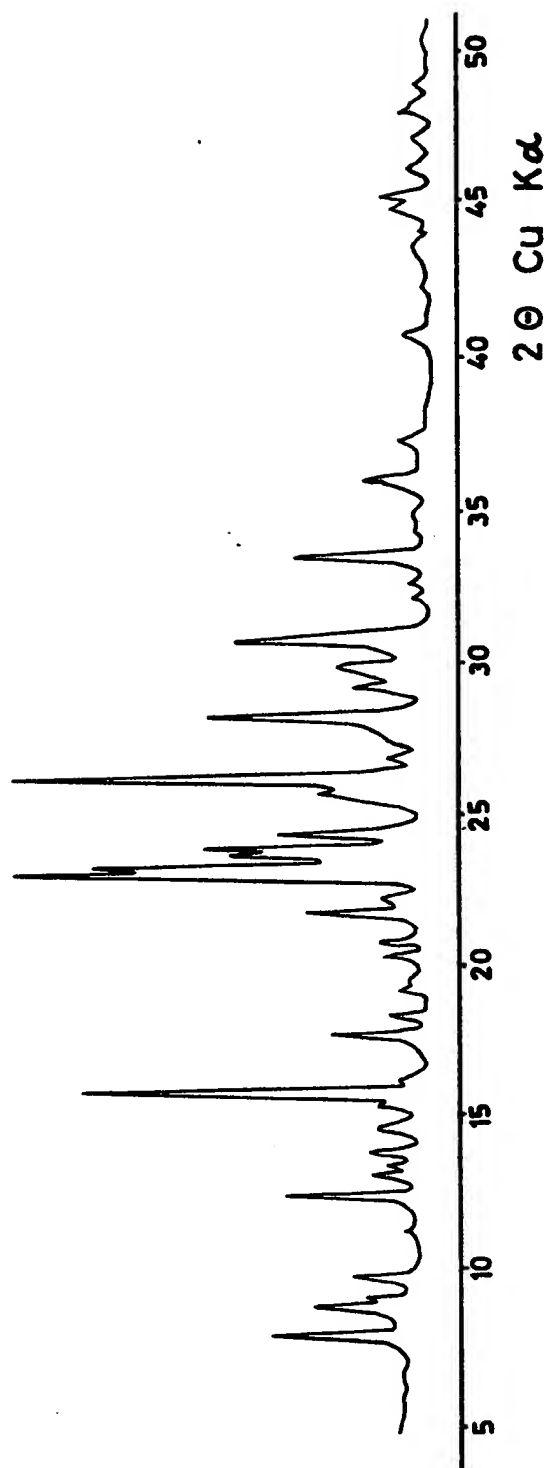
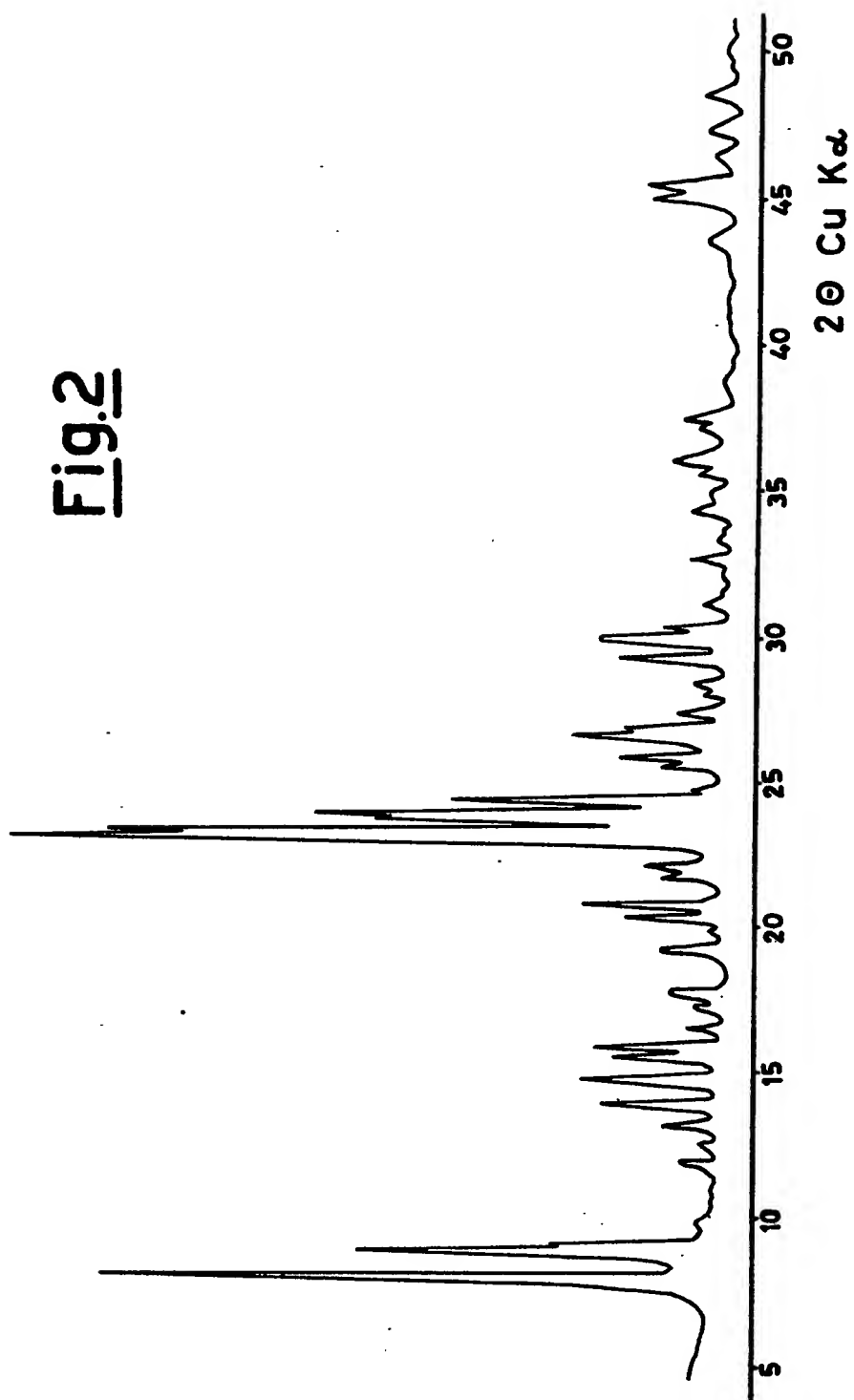


Fig.2

## SPECIFICATION

## Modified silica and germania and their use as catalysts

This invention relates to a crystalline silica or germania modified with aluminium or gallium.

Many materials based on silica and alumina, both natural and synthetic, are known. More particularly, there are known materials called zeolites, which have absorbent, molecular sieve and catalytic properties. Such materials have a content of alumina relative to silica which varies within a wide range. The maximum silica/alumina ratio is 100:1, but this ratio is generally much smaller and is preferably in the neighbourhood of 2.

These materials, which contain aluminium in tetrahedral coordination as replacement for silicon, must possess, to be electrically neutral, cations capable of balancing the charges due to the presence of the tetrahedrally coordinated aluminium atoms.

The protonic acidity of such zeolites can be attributed to the hydrogen atoms which have been introduced to exchange such cations. On the other hand, crystalline silicas, due to their intrinsic nature, do not possess protonic charges so that they cannot display any acidic character, other than that inherent in the silicic acid.

A number of crystalline silicas such as cristobalite, tridymite and keatite are known. They are prepared according to procedures which have been widely disclosed by the scientific literature. For example Heidemann, in Beitr. Min. Petrog., 70, 242 (1964) describes the reaction of an amorphous silica with 0.55% KOH at 180°C for 2½ days, whereby there is obtained a crystalline silica, called silica X, which has, however, a specific surface area of about 10 m²/g and a poor stability since it changes to cristobalite within five days and subsequently changes to quartz. More recently, Flanigen et al, Nature, 271, 512 (1978) have described a crystalline silica, namely silicalite, which has a high specific surface area and which, due to its hydrophobic properties may be used for the purification of water polluted by organic substances.

According to the present invention, there is provided aluminium-modified or gallium-modified silica or germania having a porous crystalline structure and a specific surface area greater than 150 m²/g, and having one of the following general formulae:



wherein y is from 2.0018 to 2.0075.

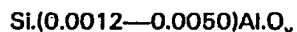
The present invention also provides a process for preparing aluminium-modified or gallium-modified silica or germania, which comprises reacting a derivative of silicon (or germanium) and a derivative of aluminium (or gallium) with a substance having an archivolt or clathrating effect, the reaction being carried out in an aqueous medium, an alcoholic medium or an aqueous alcoholic medium; crystallising the reaction mixture at a temperature of from 100° to 220°C; cooling the reaction mixture; separating the precipitate formed in the reaction mixture; and firing the precipitate in air at a temperature of from 300° to 700°C.

It had surprisingly been found in one aspect of the invention that it is possible to obtain materials having a very high silica-to-alumina ratio but which cannot be zeolites since the minimum amounts of aluminium contained therein cannot sustain a structure of the crystalline silicoaluminate type. On the other hand, these materials differ from crystalline silicas in that the introduction of tiny amounts of aluminium induces a wide variation of acidity. Such materials possess a protonic acidity equal to, or greater than, that of the protonic forms of the zeolites themselves while maintaining the very high structural stability of crystalline silica, contrary to what is experienced for the protonic forms of zeolites A, X, Y (the only exception being that of the mordenite family) which are rather labile as they tend to be readily converted into the stabler silica aluminas.

The silica aluminas, as such, possess an acidity which is somewhat lower. For example, a commercial silica alumina containing 25% by wt of alumina has a proton content, in milliequivalents (meq) per gram of catalyst, of the order of  $1 \times 10^{-3}$ .

It has been surprisingly found, furthermore, that by properly metering the quantity of aluminium in the materials, it is possible to adjust the acidity thereof so as to adapt it for the reaction for which the material is to be employed.

The silica modified by the introduction of aluminium atoms has the following general formula:



wherein y is from 2.0018 to 2.0075.

Depending upon the calcination (firing) temperature, greater or smaller amounts of water of crystallisation may be present.

To prepare the aluminium-modified silica of the present invention, it is preferred to use the following procedure:

A derivative of silicon and a derivative of aluminium are reacted in an aqueous, alcoholic or hydro-alcoholic solution with a substance having a clathrating or archivolt action, possible in the presence of one or more mineralising agents to encourage crystallisation, and possibly in the presence of an inorganic base. The resultant mixture is allowed to crystallise in an enclosure for a period of time of from

5 a few hours to many days at a temperature of from 100°C to 220°C, preferably at a temperature from 150°C to 200°C for a week. The mixture is allowed to cool and, upon collection on a filter, drying and firing at a temperature of from 300°C to 700°C, preferably at 550°C, for a time of from 2 hours to 24 hours, is carried out. The product is washed to remove the possibly exchangeable cationic impurities with boiling distilled water which contains an ammonium salt dissolved therein, preferably ammonium  
10 nitrate or ammonium acetate. The product is then fired again as above. 10

The derivative of silicon is preferably a silica gel (no matter how obtained) or a tetraalkyl orthosilicate such as tetraethyl orthosilicate or tetramethyl orthosilicate. The derivative of aluminium is preferably a salt of aluminium such as the nitrate or acetate.

The substance which displays an archivolt or clathrating action is preferably a tertiary amine, an  
15 aminoalcohol, an aminoacid, a polyhydric alcohol or a quaternary ammonium base such as a tetraalkylammonium base (e.g.  $\text{NR}_4\text{OH}$  wherein R is an alkyl radical having from 1 to 5 carbon atoms) or a tetraarylammonium base (e.g.  $\text{NA}_4\text{OH}$  wherein A is a phenyl or an alkylphenyl radical). 15

The substance having an archivolt action has the function of originating a crystalline structure with pores having a determined size, and thus is generally large molecules.

20 The mineralising agent is preferably an alkali metal or alkaline earth metal hydroxide or halide, for example  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KBr}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{CaI}_2$  or  $\text{CaBr}_2$ . The inorganic base is preferably an alkali metal or an alkaline earth metal hydroxide (e.g.  $\text{NaOH}$ ,  $\text{KOH}$  and  $\text{Ca(OH)}_2$ ) or ammonia. 20

As regards the amount of the inorganic base and/or of the clathrating substance to be used, these amounts are generally lower than the stoichiometric amount relative to silica and are preferably from  
25 0.05 to 0.50 mol per mol of silica. 25

The products are characterised by an acidity of the protonic type which can be varied by varying the silicon replacing cation which is introduced. For pure silica the number of milliequivalents of hydrogen ions per gram is  $1 \times 10^{-3}$ . This acidity can be increased by the introduction of aluminium until the number of milliequivalents of hydrogen ions per gram is about  $1 \times 10^{-1}$ .

30 The materials according to the present invention are characterised by a well defined crystalline structure as can be seen in the X-ray diffraction spectra given in Figures 1 and 2 of the accompanying drawings and possess a high specific surface area which is over 150  $\text{m}^2/\text{g}$  and is generally from 300  $\text{m}^2/\text{g}$  to 500  $\text{m}^2/\text{g}$ . 30

The presence of aluminium, which modifies the acidity of the silica, gives rise to the formation of  
35 crystalline materials the spectra of which can either be very similar to those reported in the literature for the crystalline silica called silicate (Nature, 271, 512 (1978)), or, conversely, be remarkably different therefrom. 35

The aluminium-modified silica according to the invention can be employed for catalytic or absorption uses, either as such or when dispersed on a supporting body which is inert to a lesser or  
40 greater extent and which has a high or low specific surface area and porosity. 40

The supporting body improves the physical and mechanical stability and possibly also the catalytic properties of the material. The procedures used for obtaining supported materials are known in the art.

The amount of supporting body is generally from 1% to 90%, amounts of from 5% to 60% being preferred. The preferred supporting bodies are clays, silica, alumina, diatomaceous earth and silica-  
45 alumina. 45

The aluminium-modified silica according to this invention can be employed as a catalyst for a large number of reactions among which are the alkylation of benzene, more particularly the alkylation of benzene with ethylene and the alkylation of benzene with ethanol. Examples of other uses are:

- (1) Alkylation of toluene with methanol to produce xylene, predominantly p-xylene;
- 50 (2) Disproportionation of toluene to produce predominantly p-xylene; 50
- (3) Conversion of dimethyl ether and/or methanol or other lower alcohols to hydrocarbons (olefins and aromatics);
- (4) Cracking and hydrocracking;
- (5) Isomerisation of normal paraffins and naphthenes;
- 55 (6) Polymerisation of compounds which contain olefinic or acetylenic bonds; 55
- (7) Reforming;
- (8) Isomerisation of polyalkyl substituted aromatic hydrocarbons such as o-xylene;
- (9) Disproportionation of aromatic hydrocarbons, especially toluene;
- (10) Conversion of aliphatic carbonyl compounds into at least partially aromatic hydrocarbons;
- 60 (11) Separation of ethylbenzene from other  $\text{C}_8$  aromatic hydrocarbons; 60
- (12) Hydrogenation and dehydrogenation of hydrocarbons;
- (13) Methanation;

The foregoing description relates to aluminium-modified silica. However, gallium can be substituted for the aluminium and germanium can be substituted for the silicon.

In a preferred embodiment of the invention, the catalysts of the invention are used in the alkylation of  $C_4$  hydrocarbons, olefins and/or saturated hydrocarbons (paraffins), to form hydrocarbons having high octane numbers. As outlined above, the catalysts are porous and have a specific surface area greater than  $150 \text{ m}^2/\text{g}$ .

5 In a modification, the present invention relates to the preparation and use of a zeolite-type catalyst of the class ZSM-5. 5

It is known from U.S. Patent Specification No. 3 702 886 that zeolites of the class ZSM-5 can be prepared from derivatives of silicon (such as silica sols, aerosol-type amorphous silicas or tetraalkyl orthosilicates) or derivatives of aluminium (such as sodium aluminate, aluminium sulphate and

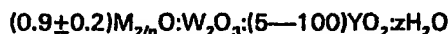
10 aluminium acetate) and from quaternary ammonium bases such as tetrapropylammonium hydroxide. 10

According to a modified embodiment of the present invention it has been ascertained that zeolites of the ZSM-5 type can be prepared by the general teachings of the invention, whenever the material which monitors the crystallisation is an aminoalcohol and by the use of amounts of compounds of silicon, germanium, aluminium and gallium such that the molar ratios

15  $\text{SiO}_2:\text{Al}_2\text{O}_3:\text{GeO}_2:\text{Al}_2\text{O}_3:\text{SiO}_2:\text{Ga}_2\text{O}_3:\text{GeO}_2:\text{Ga}_2\text{O}_3$  15

are between 5 and 100 and are preferably in the vicinity of 35.

A zeolite prepared according to the present invention has an X-ray diffraction spectrum akin to that of zeolite ZSM-5 and has the general formula:



20 wherein M is a cation selected from  $\text{H}^+$  and/or  $\text{NH}_4^+$  and/or metallic cations and/or cations deriving from amino alcohols (especially ethanolamines),  $n$  is the valency of the cation, W is aluminium or gallium, Y is silicon or germanium and  $z$  is from 0 to 40. 20

In a preferred form of this zeolite, W is aluminium, Y is silicon and the ratio of silica to alumina is from 10 to 60.

25 The preparation of the preferred zeolite according to the present invention is carried out by admixing the reactants in the following ratios, expressed in terms of mols of oxides: 25

Ratios	Broad Range	Preferred Range	
$\text{OH}^-/\text{SiO}_2$	0.2— 0.8	0.3— 0.6	
$\text{T.E.T.A.}/\text{T.E.T.A.} + \text{Na}^+$	0.3— 0.8	0.4— 0.6	
30 $\text{H}_2\text{O}/\text{OH}^-$	10 —100	20 —40	30

wherein T.E.T.A. is an amino alcohol, more particularly triethanolamine.

The process according to this particular aspect of the present invention is preferably carried out as follows:

A derivative of silicon or of germanium and a derivative of aluminium or gallium is reacted, in an aqueous, alcoholic or hydroalcoholic solution, with an amino alcohol (such as an ethanolamine and more particularly triethanolamine), possibly in the presence of one or more mineralising agents such as hydroxides and/or halides of alkali metals or alkaline earth metals to encourage crystallisation. The mixture is allowed to crystallise in an enclosure for a period from a few hours to many days at a high temperature of from  $150^\circ\text{C}$  to  $250^\circ\text{C}$  and preferably from  $170^\circ\text{C}$  to  $210^\circ\text{C}$  for a period of time of from 2 to 10 days, generally one week, allowed to cool and, upon collection on a filter and washing with deionised water, the crystals are dried and fired in air at a temperature of from  $300^\circ\text{C}$  to  $700^\circ\text{C}$ , preferably at  $550^\circ\text{C}$ , for a period of from 2 hours to 24 hours. Thereafter a repeated cationic exchange is effected with an ammonium salt, preferably ammonium nitrate or acetate. Washing with distilled water and firing once again as described above is carried out if the product is desired in the  $\text{H}^+$  form.

45 The zeolite thus prepared can be used as such, or diluted in an appropriate dilution ratio and supplemented with one or more elements having catalytic promoting activity, according to the procedures and other methods provided for the zeolites of the ZSM-5 class. 45

The invention will now be illustrated by the following Examples:

#### EXAMPLE 1

50 This Example illustrates the preparation of a porous crystalline silica in the crystalline lattice of which aluminium has been introduced as silicon-replacing element. This modified silica has been designated by us as catalyst "TRS-22". 50

A Pyrex (Registered Trade Mark) glass vessel kept in a nitrogen atmosphere was charged with 80 g of tetraethyl orthosilicate. The silicate was heated with stirring to a temperature of  $80^\circ\text{C}$ . There were added a solution, in 80 ml of distilled water, of 20 g of tetrapropylammonium hydroxide (obtained from tetrapropylammonium and moistened silver oxide so that it was free of inorganic alkaline bases). Stirring was continued at  $80^\circ\text{C}$ , until the mixture was homogeneous and clear. This took about one hour. 55

There were added 80 mg (milligrams) of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  dissolved in 50 ml of absolute ethanol. A compact gel formed almost immediately, and distilled water was added thereto to make up to an overall volume of 200 ml, stirring being carried out if necessary. The mixture was brought to a boil so as to complete the hydrolysis and to drive off all the ethanol, i.e. that added and that formed by the hydrolysis.

5 The time taken by these steps was from 2 to 3 hours and the gel was converted, slowly and gradually, into a white powder, which is the precursor of the modified crystalline silica. 5

The mixture was made up to 150 ml with distilled water and the vessel was kept in an autoclave at a temperature of 155°C for 7 days. Upon cooling, the solid which had formed was centrifuged at a speed of 10,000 rpm for 15 minutes. It was reslurried in distilled water and centrifuged once more. 10 washing step was repeated four times. The product was oven dried at 120°C. It was X-ray crystalline. 10

The product, dried at 120°C, contained 83.0% by wt of  $\text{SiO}_2$ , 0.2% by wt of  $\text{Al}_2\text{O}_3$ , 0.18% by wt of  $\text{Na}_2\text{O}$  and 0.02% by wt of  $\text{K}_2\text{O}$ . Its loss on firing at 1100°C was 16.6%, and its molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 704:1. The alkali metals present came from the reactants and from the glass, since they were not deliberately added.

15 In order to completely remove the alkaline impurities, the product was fired for 16 hours at 550°C in an air stream, was repeatedly washed with boiling distilled water containing ammonium acetate dissolved therein, and was fired again at 550°C for 6 hours. Its specific surface area, as determined by the BET method, was 444  $\text{m}^2/\text{g}$ . Its concentration of protons in milliequivalents per gram of sample was  $1.5 \times 10^{-1}$ . 15

## 20 EXAMPLE 2 20

This Example illustrates the preparation of a porous crystalline silica in the crystalline lattice of which traces of aluminium have been introduced as a replacement for the silicon. This modified silica has been designated by us as catalyst "TRS-O".

A Pyrex glass flask equipped with a reflux condenser and maintained in a nitrogen atmosphere 25 was charged with 40 G of tetraethyl orthosilicate and 120 ml of a 20% by wt aqueous solution of tetrapropylammonium hydroxide. The mixture was heated to boiling point. The final result was a clear, colourless solution which remained limpid even after refluxing for a long time. 25

There were added 30 mg of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , whereupon the solution became opalescent and, by continuing the application of heat, a white powder separated therefrom.

30 Boiling was continued for 6 days, whereafter the mixture was allowed to cool, the solid product was collected on a filter and washed with distilled water and dried at 100°C. The product, dried at 100°C, was X-ray crystalline. It was fired for 16 hours at 550°C in an air stream and was subsequently repeatedly washed with boiling distilled water which contained ammonium acetate dissolved therein. Thereafter, the product was fired at 550°C once more for 6 hours. 30

35 The product thus obtained contained 96.2% wt of  $\text{SiO}_2$ , 0.2% wt of  $\text{Al}_2\text{O}_3$  and 0.02% wt of  $\text{Na}_2\text{O} + \text{K}_2\text{O}$ . Its weight loss on firing at 1100°C was 3.58% and its molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 816:1. 35

The traces of alkali metals which were present come from the reactants and the glass since they were not deliberately added. The specific surface area of the product, as determined by the BET method, 40 was 420  $\text{m}^2/\text{g}$ . Its content of protons in milliequivalents per gram was  $1.9 \times 10^{-1}$ . 40

## EXAMPLE 3

This Example illustrates the preparation of a porous crystalline silica, designated by us as catalyst "TRS-23", in the crystalline lattice of which aluminium has been introduced as a replacement for silicon and in the preparation of which there was used an organic base, namely tetraethylammonium 45 hydroxide, different from the base used in Examples 1 and 2. 45

The procedure of Example 1 was employed, using 80 g of tetraethyl orthosilicate, 68 ml of a 25% by wt aqueous solution of tetraethylammonium hydroxide, 80 mg of  $\text{Al}_2(\text{NO}_3)_6 \cdot 9\text{H}_2\text{O}$  dissolved in 50 ml of absolute ethanol and 2 g of NaOH pellets dissolved in 10 ml of distilled water, this mixture being maintained at a temperature of 155°C for 18 days.

50 The product, when dried at 120°C, was X-ray crystalline. Its content of protons in milliequivalents per gram after firing was  $1.1 \times 10^{-2}$ . 50

A thoroughly washed sample which had been fired at 550°C contained 96.3% by wt of  $\text{SiO}_2$ , 0.2% by wt of  $\text{Al}_2\text{O}_3$  and 0.03% by wt of  $\text{Na}_2\text{O}$ . Its weight loss on firing at 1100°C was 3.47%, its molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 816:1, its specific surface area, as determined by the BET method, was 470  $\text{m}^2/\text{g}$ , 55 and its content of protons in milliequivalents per gram was  $4.3 \times 10^{-3}$ . 55

## EXAMPLE 4

This Example illustrates the preparation of a porous crystalline silica, designated by us as catalyst "TRS-19", in the crystalline lattice of which aluminium has been introduced as a replacement for silicon and in the preparation of which there is used an organic base, namely tetrabutylammonium hydroxide, 60 different from those used in the previous Examples. 60

The procedure of Example 1 was employed, using 50 g of tetraethyl orthosilicate, a solution of 100 mg of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 50 ml of absolute ethanol, a solution of 29 g of tetrabutylammonium

hydroxide (obtained from tetrabutylammonium bromide and moistened silver oxide) in 120 ml of distilled water and 2 g of NaOH dissolved in 20 ml of distilled water. This mixture was placed in an autoclave and held for 16 days at a temperature of 155°C. The product, dried at 120°C, was X-ray crystalline. Its content of protons in milliequivalents per gram, after firing at 550°C, was  $4.5 \times 10^{-4}$ .

5 A thoroughly washed sample contained 96.0% by wt of  $\text{SiO}_2$ , 0.3% by wt of  $\text{Al}_2\text{O}_3$  and 0.03% by wt of  $\text{Na}_2\text{O}$ . Its weight loss on firing at 1100°C was 3.67%, its molar ratio  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 543:1, its specific surface area, as measured by the BET method, was 380  $\text{m}^2/\text{g}$ , and its content of protons in milliequivalents per gram was  $2.5 \times 10^{-1}$ .

Figure 1 of the accompanying drawings shows the X-ray diffraction spectrum of the product.

#### 10 EXAMPLE 5

This Example illustrates the preparation of a porous crystalline silica, designated by us as catalyst "TRS-20", in the crystalline lattice of which aluminium has been introduced as a modifying element in place of silicon. The preparation of this silica was carried out without any inorganic alkaline base being present, the only alkaline cations present being those present as impurities in the reactants.

15 By the procedure of Example 1, there were reacted 40 g of tetraethyl orthosilicate, a solution of 100 mg of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in 50 ml of absolute ethanol, 50 ml of a 40% by wt aqueous solution of tetrapropylammonium hydroxide (obtained from tetrapropylammonium bromide and moistened silver oxide), to obtain a product free of alkaline inorganic bases. The mixture was maintained at 155°C for 10 days.

20 X-ray analysis indicated the crystalline character of the product dried at 120°C. For use as a catalyst, the product was fired at 550°C in air for 16 hours and then repeatedly washed with boiling distilled water containing dissolved therein ammonium acetate. The product was fired once again at 550°C for 6 hours.

25 The product thus obtained contained 96.1% by wt of  $\text{SiO}_2$ , 0.3% by wt of  $\text{Al}_2\text{O}_3$  and 0.01% by wt of  $\text{Na}_2\text{O}$ . Its weight loss on firing at 1100°C was 3.59%, its molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 544:1, its specific surface area as determined by the BET method was as high as 500  $\text{m}^2/\text{g}$ , and its concentration of  $\text{H}^+$  ions per gram was  $4.7 \times 10^{-1}$  meq.

#### EXAMPLE 6

30 This Example illustrates the preparation of a porous crystalline silica, designated by us as catalyst "TRS-57", in the crystalline lattice of which aluminium has been introduced as the modifier. In the preparation of the silica, triethanolamine was used.

There were reacted 80 g of tetraethyl orthosilicate, 80 mg of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  dissolved in 50 ml of absolute ethanol, a solution of 27 g of triethanolamine in 50 ml of distilled water, the procedure being disclosed in Example 1. There were added 7 g of sodium hydroxide and the Pyrex glass vessel was 35 placed in an autoclave and maintained at a temperature of 194°C for 7 days.

It was ascertained that the product, dried at 120°C, was X-ray crystalline. The X-ray diffraction spectrum of the product is shown in Figure 2 of the accompanying drawings.

40 The product, fired at 550°C, contained 96.2% by wt of  $\text{SiO}_2$ , 0.2% by wt of  $\text{Al}_2\text{O}_3$  and 0.05% by wt of  $\text{Na}_2\text{O}$ . Its weight loss on firing at 1100°C was 3.55%, its molar ratio of  $\text{SiO}_2$  to  $\text{Al}_2\text{O}_3$  was 816:1, its specific surface area, measured by the BET method, was 344  $\text{m}^2/\text{g}$ , and its content of  $\text{H}^+$  in meq per gram was  $1.5 \times 10^{-1}$ .

#### EXAMPLE 7 (Comparative Example)

This Example illustrates the lack of dehydrating catalytic properties of the modified crystalline silica TRS-22 prepared according to Example 1, but containing sodium cations, so that its content of 45 protons in milliequivalents per gram was as low as  $4.1 \times 10^{-4}$ .

The formation of dimethyl ether from methanol was used as the exemplary dehydration reaction. An electrically heated tubular reactor having an inside diameter of 8 mm was charged with 4 ml (2 g) of catalyst having a size of from 30 to 80 mesh (ASTM series).

50 A sample of the effluent of the reaction was taken downstream of the reactor and analysis was carried out gaschromatographically.

The catalyst was initially fired at 500°C for two hours in a nitrogen stream to remove the absorbed water, methanol was then fed in at a weight hourly space velocity (WHSV) of 1.5 g/g an hour, using an oven temperature of 275°C and subsequently of 400°C. Analysis of the reaction effluent showed the presence of methanol only at both temperatures.

#### 55 EXAMPLE 8 (Comparative Example)

This Example illustrates the absence of dehydrating properties of the modified crystalline silica TRS-23 prepared according to Example 3 and not thoroughly washed so that its content of protons in milliequivalents per gram was as low as  $1.1 \times 10^{-6}$ .

60 The procedure and the apparatus of Example 7 was used. The reactor was charged with 4 ml (2.8 g) of catalyst the grit size of which was from 30 to 80 mesh (ASTM series), and the catalyst was heated for two hours at 500°C in a stream of anhydrous nitrogen.



Methanol was fed in at a temperature of 240°C, 300°C and 400°C at a WHSV of 1.75 grams per gram an hour. In all three cases, no dimethyl ether was found in the reaction effluent, i.e. methanol only was found.

#### EXAMPLE 9

5 This Example illustrates the excellent catalytic dehydrating properties of the modified crystalline silica TRS-22 prepared according to Example 1 and having a content of protons in milliequivalents per gram of  $1.5 \times 10^{-1}$ . The procedure and apparatus of Example 7 was used. The reactor was charged with 5 ml (3.5 g) of catalyst having a grit size of from 30 to 80 mesh (ASTM series). 5

After firing the catalyst for 2 hours under an anhydrous nitrogen stream to remove the adsorbed water, methanol was fed in at WHSV of 1.5 g/g per hour at reactor temperatures of 250°C and 265°C. 10

Analysis of the reactor effluent, which consisted of dimethyl ether, unreacted methanol and water without the presence of by-products detectable by gas chromatography, gave the results tabulated in Table 1 below.

15 It can be seen that the crystalline silica has an excellent dehydrating activity, with conversion percentages even higher than those described in Patent Specification No. 1,492,276. 15

By using TRS-22 at 250°C and at 265°C, there are obtained, at a WHSV of 1.5, conversions of methanol which are, respectively, equal to and higher than those which can be obtained at 300°C and at a WHSV of 1, using active alumina which has been treated with silicon compounds.

#### EXAMPLE 10 (Comparative Example)

20 This Example illustrates the conversion of dimethyl ether into hydrocarbons, particularly light olefins, using modified crystalline silica TRS-22 prepared according to Example 1 and containing sodium cations, the content of protons in milliequivalents per gram of catalyst being  $4.1 \times 10^{-4}$ . 20

An electrically heated tubular reactor having an inside diameter of 8 mm was charged with 2 ml (1 g) of the catalyst having a grit size between 30 and 80 mesh (ASTM series).

25 The catalyst was heated to 550°C for 2 hours in a nitrogen stream to remove absorbed water, if any. Gaseous dimethyl ether was fed in while heating all of the pipes to prevent condensation. Downstream of the reactor, a heated sampling appliance was installed, to permit the introduction of the reactor effluent into a gaschromatograph in which analysis of the reaction products is carried out. 25

As regards the calculation of the conversion, it is to be borne in mind that the methanol which is 30 formed by partial hydration of the dimethyl ether is considered as an unreacted product, so that the molar conversion is based on the dimethyl ether which has been converted into hydrocarbons, carbon monoxide and carbon dioxide. The molar selectivities on the products are referred to the number of mols of dimethyl ether which have been converted into the indicated product, relative to the total number of reacted mols. The results obtained are tabulated in Table 2 below. The Table clearly shows that the 35 catalyst is not very active and not very selective, inasmuch as considerable amounts of carbon monoxide and carbon dioxide and methane are formed. 35

#### EXAMPLE 11

This Example illustrates the conversion of dimethyl ether into hydrocarbons, particularly light olefins, using the modified crystalline silica TRS-22 prepared according to Example 1 having a 40 concentration of protons of  $1.5 \times 10^{-1}$  milliequivalents per gram. 40

The procedure and the apparatus of Example 9 was used. The reactor was charged with 3 ml (1.5 g) of catalyst having a grit size of from 30 to 80 mesh (ASTM series).

The catalyst had previously been heated to 550°C for 2 hours in a nitrogen stream to remove absorbed water.

45 The results obtained are tabulated in Table 3 below. Comparison with Table 2 clearly shows that, as the acidity is varied, the behaviour of the catalyst is improved. 45

#### EXAMPLE 12

This Example illustrates the activity, in the alkylation of benzene with ethylene, of catalyst TRS-22 ( $1.5 \times 10^{-1}$  meq  $H^+$  per gram).

50 An electrically heated tubular reactor having an inside diameter of 8 mm was charged with 1.2 ml (0.8 g) of catalyst TRS-22 having a grit size of from 30 to 50 mesh. By use of a metering pump, benzene was first passed through a preheater system wherein it mixed with ethylene of a preselected rate of flow. The mixture was passed into the reactor. The pressure was 20 kg/cm<sup>2</sup>, the LHSV was 14 and the molar ratio of  $C_6H_6$  to  $C_2H_4$  was 7:1. The reaction products were gaschromatographically analysed. Table 4 55 tabulates the results obtained. 55

#### EXAMPLE 13

This Example illustrates the regeneration of the catalyst used in the previous Example. After 400 hours of operation, the catalyst was regenerated at 550°C in a properly adjusted air stream for 5 hours.

60 On completion of the regeneration, the system was purged with nitrogen for one hour, still at 550°C, whereafter the reaction was restarted under the same conditions as reported previously. Table 5 below gives the results obtained. 60

**EXAMPLE 14**

This Example illustrates the activity, in the alkylation of benzene with ethanol, of catalyst TRS-0.

An electrically heated tubular reactor having an inside diameter of 8 mm was charged with 1.2 ml (0.8 g) of the catalyst having a grit size of from 30 to 50 mesh. By use of a metering pump, the reaction mixture, which consisted of benzene and ethanol in a molar ratio of 5:1 were introduced first into a preheater and then into the reactor.

The reaction is carried out at 440°C, at a pressure of 20 Kg/cm<sup>2</sup>, at a LHSV of 10 and using a molar ratio of C<sub>6</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>5</sub>OH of 4:1. The reaction products were gaschromatographically analysed. The results obtained are given in Table 6.

**EXAMPLE 15**

5 ml of the aluminium-modified silica TRS-20 prepared as in Example 5 were impregnated with an aqueous solution of H<sub>2</sub>PtCl<sub>6</sub> such that the content of platinum in the catalyst was 0.2% by wt. The platinum was reduced to the elemental state at 600°C in a hydrogen stream, the catalyst was introduced into an electrically heated tubular reactor having an inside diameter of 20 mm.

The ability of the catalyst to purify the exhaust gases of a motor car was determined with two typical reactions, namely oxidation of propylene to carbon dioxide and oxidation of carbon monoxide to carbon dioxide.

**Test A**

A gas consisting of 800 ppm of propylene, 8% of oxygen and the balance nitrogen was preheated to 120°C and passed over the catalyst at a Gaseous Hourly Space Velocity (GHSV) of 50,000 hours<sup>-1</sup> (reciprocal hours). The conversion of propylene was 99%. The same gaseous mixture, preheated to 90°C, was fed over the catalyst at a GHSV of 20,000 hours<sup>-1</sup>, and a conversion of 99% of the propylene was obtained.

**Test B**

A gas consisting of 2.5% of CO, 8% of oxygen and the balance nitrogen was preheated to 80°C and passed over the catalyst at a GHSV of 20,000 hours<sup>-1</sup>. The conversion of CO was 59%.

The same gaseous mixture, preheated to the same temperature, was fed over the catalyst at a GHSV of 50,000 hours<sup>-1</sup>, and the conversion of CO was 99%.

The temperatures above, i.e. from 80°C to 120°C, must be correctly regarded as exceptional since the best commercial catalyst as used in catalytic silencers can effect the same conversions of propylene and carbon dioxide at the same space velocities, but only at temperatures above 150°C.

**EXAMPLE 16**

This Example illustrates the activity, in the alkylation of benzene with ethylene, of catalyst TRS-57 prepared according to Example 6.

The reaction was carried out in a tubular reactor of the fixed-bed type, having an inside diameter of 8 mm and being electrically heated. There was introduced into the reactor, 1.2 ml (0.85 g) of the catalyst, having a grit size of from 30 to 50 mesh. By use of a metering pump, benzene was introduced, first into a preheater system (where it merges with a preselected rate of flow of ethylene) and then into the reactor. The reaction was carried out at a pressure of 20 kg/cm<sup>2</sup>, at a temperature of 440°C, at a LHSV of 14 and using a molar ratio of C<sub>6</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>4</sub> of 7:1. The reactor effluent was gaschromatographically analysed. Table 7 below gives the results obtained.

**EXAMPLE 17**

The catalyst which had been used for the reaction of Example 16 was subjected to an in situ regeneration using a stream of air diluted with nitrogen at 500°C.

On completion of the regeneration, the catalyst was again used for the alkylation of benzene with ethylene, under the same conditions. The results tabulated in Table 8 below are a clear indication of how simple and advantageous it is to regenerate the catalyst.

**EXAMPLE 18**

This Example illustrates the activity of catalyst TRS-57 as described in Example 6 in the alkylation of benzene with ethanol.

The reaction was carried out in an electrically heated, fixed-bed, tubular reactor, into which 1.2 ml (0.85 g) of the catalyst, having a grit size of from 30 to 50 mesh, had been introduced. Via a metering pump, the reaction mixture, namely benzene and ethanol, was introduced first into a preheater assembly and then into the reactor. The reaction was carried out at a pressure of 20 kg/cm<sup>2</sup>, at a temperature of 440°C, at a LHSV of 10 and using a molar ratio of C<sub>6</sub>H<sub>6</sub> to C<sub>2</sub>H<sub>5</sub>OH of 5:1. The effluent was gaschromatographically analysed. Table 9 below gives the results obtained.

**EXAMPLE 19**

For alkylating isobutene with normal butenes, a porous crystalline silica, as obtained in Example 5, in the crystalline lattice of which aluminium has been introduced as a replacement for silicon, was employed as the catalyst.

A small reactor as described in Example 7 was charged with 3 ml (1.9 g) of the catalyst, having a grit size of from 30 to 50 mesh.

The pressure used was 20 kg/cm<sup>2</sup> and the molar ratio of isobutene to normal butene was 15:1. The other conditions used and the results obtained are tabulated in Table 10 below.

#### 5 EXAMPLE 20

This Example illustrates the preparation of zeolite ZSM—5, using triethanolamine.

A Pyrex glass vessel maintained in a CO<sub>2</sub>-free atmosphere was charged with 60 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O dissolved in 400 ml of 95% ethanol. There were added with stirring 600 g of tetraethyl orthosilicate. As soon as the solution became limpid, there were added 200 g of triethanolamine dissolved in 400 ml of distilled water and the mixture was heated, still with stirring, to 60°C. After 30 additional minutes, there was added a solution of 13 g of NaOH in 200 ml of distilled water, and after a further 30 minutes, there were added 22 g of NaOH dissolved in 400 ml of water, the total amount of NaOH therefore being 35 g. Massive formation of gel was observed. Vigorous stirring was carried out for a few hours, while at the same time the temperature was raised to 90°C so as to dispel all of the ethanol, i.e. both that introduced into the reaction and that formed by the hydrolysis. At this stage, the reaction mixture was transferred to a 3-litre stainless steel autoclave and hydrothermal treatment at 195°C for 9 days was carried out.

The resulting product was then allowed to cool to room temperature, collected on a filter, washed many times with very hot distilled water, and dried at 120°C. The solid product was then fired at 550°C for 16 hours, and was converted to the H<sup>+</sup> form by repeated exchange while hot (95°C) with ammonium acetate or nitrate and by firing again at 550°C for 6 hours. The X-ray diffraction spectrum of the product corresponds to that reported in Table 1 of the U.S. Patent Specification No. 3 702 886.

#### EXAMPLE 21

By the procedure of Example 20, there were reacted 880 g of tetramethyl orthosilicate, 120 g of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O, 400 g of triethanolamine which had previously been dissolved in 800 ml of water, 70 g of NaOH in 700 ml of water. The mixture was made up to a volume of about 9 litres by adding distilled water with very vigorous stirring. The mixture was concentrated at a temperature of 80°C for about 30 hours until its volume was reduced to about 5 litres. Hydrothermal treatment was effected for 8 days at 190°C in a stainless steel autoclave equipped with a stirrer.

The X-ray diffraction spectrum of the product corresponds to that of ZSM—5. The specific surface area of the product was 380 m<sup>2</sup>/g, and its ratio of SiO<sub>2</sub> to Al<sub>2</sub>O<sub>3</sub> was 38:1.

#### EXAMPLE 22

9.6 g of sodium aluminate and 10 g of potassium hydroxide were dissolved in 200 ml of water. To the clear solution obtained, there was added 208 g of triethanolamine dissolved in 1,000 ml of water. The solution thus obtained was allowed to stand, with stirring and under an inert gas blanket, for two hours at 80°C. There were added, as a crystallisation agent, 40 g of potassium bromide dissolved in 150 ml of water.

There were now slowly added 345 g of Ludox colloidal silica (40% SiO<sub>2</sub>) dissolved in 1,500 ml of water. The resultant gel was allowed to age for 24 hours at 90°C under an inert gas stream. The gel was then crystallised in a stainless steel autoclave for 10 days at 198 C.

The procedure described in Example 20 was carried out and zeolite ZSM-5 was obtained.

TABLE 1

Temperature (°C)	250°C	265°C
Pressure (bar)	1	1
WHSV (g/g hourly)	1.5	1.5
Conversion of CH <sub>3</sub> OH (mol %)	82.4	88.1

TABLE 2

Test	Temp. (°C)	Press. (bar)	WHSV	Conversion per pass (mol %)	Products (mol %)			
					CO + CO <sub>2</sub> + CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>2</sub> H <sub>6</sub>	C <sub>4</sub> <sup>+</sup>
1	375	1	0.65	2.3	5.0	14.9	30.1	50.0
2	475	1	0.20	97.0	10.9	6.5	26.1	56.5

TABLE 3

Test	Temp. (°C)	Press. (bar)	WHSV	Conversion per pass (mol %)	Products (mol %)			
					CO + CO <sub>2</sub> + CH <sub>4</sub>	C <sub>2</sub> H <sub>4</sub>	C <sub>3</sub> H <sub>6</sub>	C <sub>4</sub> <sup>+</sup>
1	305	1	2.7	38.8	0.5	30.1	24.3	45.1
2	335	1	2.7	87.9	0.5	23.0	19.9	56.6
3	365	1	4.7	97.3	0.5	19.0	18.8	61.7
4	365	1	6.7	87.4	0.5	23.2	19.7	56.6
5	485	1	6.7	97.1	0.5	18.3	18.7	61.9
6	485	1	8.7	87.1	0.5	20.1	18.2	61.2
7	440	1	9.0	92.1	0.5	16.5	15.2	67.8

TABLE 4

Run (hours)	Temp. (°C)	Mol % of ethylbenzene in product	Mol % of diethylbenzene in product	Conversion of ethylene (%)
10	440	13.8	1.50	100.0
50	440	13.7	1.55	100.0
100	440	13.9	1.45	100.0
150	440	13.9	1.45	100.0
200	440	13.8	1.50	100.0
250	440	11.9	0.80	80.8
300	440	8.2	0.25	51.8
320	470	11.5	0.70	76.7
350	470	10.9	0.65	72.6
400	470	10.3	0.60	68.2

TABLE 5

Run (hours)	Temp. (°C)	Mol % of ethylbenzene in product	Mol % of diethylbenzene in product	Conversion of ethylene (%)
10	440	13.7	1.55	100.0
50	440	13.6	1.40	97.6
100	440	13.8	1.50	100.0
150	440	13.9	1.45	100.0
200	440	13.7	1.55	100.0
250	440	12.2	0.95	83.9
300	440	10.3	0.60	68.45
350	440	9.8	0.38	62.85

TABLE 6

Run (hours)	Mol % of ethylbenzene in product	Mol % of diethylbenzene in product	Conversion of $C_2H_5OH$ (%)
50	19.0	1.2	100
100	19.0	1.2	100
150	19.0	1.2	100
200	19.0	1.2	100
300	19.0	1.2	100
400	19.0	1.2	100

TABLE 7

Run (hours)	Mol % of ethylbenzene in product	Mol % of diethylbenzene in product	Conversion of ethylene (%)
10	13.9	1.35	100.0
50	13.9	1.35	100.0
100	14.0	1.30	100.0
150	13.8	1.30	98.8
200	13.9	1.35	100.0
250	13.7	1.28	97.9
300	12.5	1.02	87.6
350	11.3	0.90	78.9

TABLE 8

Run (hours)	Mol % of ethylbenzene in product	Mol % of diethylbenzene in product	Conversion of ethylene (%)
10	14.0	1.30	100.0
50	13.9	1.35	100.0
100	13.8	1.40	100.0
150	13.9	1.35	100.0
200	13.8	1.40	100.0
250	13.2	1.19	93.8
300	12.8	0.95	88.5

TABLE 9

Run	Mol % of ethylbenzene in the product	Mol % of diethylbenzene in the product	Conversion of C <sub>2</sub> H <sub>5</sub> OH (%)
50	18.8	1.3	100
100	19.0	1.2	100
150	18.8	1.3	100
200	19.0	1.2	100
250	19.0	1.2	100
300	19.0	1.2	100
400	19.0	1.2	100

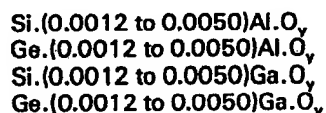
TABLE 10

Temp. (°C)	LHSV (rec. hrs)	% alkylation with respect to the butenes	Composition of the products
250	1.3	100	about 90% iso-paraffins + about 20% aromatics
350	1.3	100	about 50% iso-paraffins + about 50% aromatics
350	5.0	90	about 70% iso-paraffins + about 30% aromatics

Attention is drawn to the two applications filed by us on the same day as the present application for inventions entitled "Synthetic silica-based materials" (No. 7921622) and "Process for the preparation of tertiary olefins" (No. 7921623).

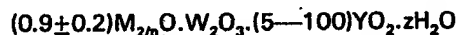
#### CLAIMS

1. Aluminium-modified or gallium-modified silica or germania having a porous crystalline structure and a specific surface area greater than 150 m<sup>2</sup>/g, and having one of the following general formulae:



wherein y is from 2.0018 to 2.0075.

2. A zeolite having the general formula:



wherein M is a cation selected from H<sup>+</sup> and/or NH<sub>4</sub><sup>+</sup> and/or metallic cations and/or cations derived from amino alcohols, n is the valency of the cation, W is aluminium or gallium, Y is silicon or germanium and z is from 0 to 40.

3. A material as claimed in claim 1 or 2, substantially as described in any of the foregoing

Examples.

4. A process for preparing aluminium-modified or gallium-modified silica or germania, which comprises reacting a derivative of silicon (or germanium) and a derivative of aluminium (or gallium) with a substance having an archvolt or clathrating effect, the reaction being carried out in an aqueous medium, an alcoholic medium or an aqueous alcoholic medium; crystallising the reaction mixture at a temperature of from 100 to 220°C; cooling the reaction mixture; separating the precipitate formed in the reaction mixture; and firing the precipitate in air at a temperature of from 300 to 700°C.

5. A process according to claim 4, wherein the reaction mixture is crystallised for a time of from a few hours to a number of days.

6. A process according to claim 4 or 5, wherein the precipitate is fired for a time of from 2 to 24 hours.
7. A process according to any of claims 4 to 6, wherein the fired product is washed with boiling water having an ammonium salt dissolved therein, and wherein the washed product is fired in air at a temperature of from 300 to 700°C.
- 5 8. A process according to claim 7, wherein the washed product is fired for a time of from 2 to 24 hours. 5
9. A process according to any of claims 4 to 8, wherein the derivation of silicon is a silica gel or a tetraalkyl orthosilicate.
- 10 10. A process according to claim 9, wherein the tetraalkyl orthosilicate is tetraethyl orthosilicate or tetramethyl orthosilicate. 10
11. A process according to any of claims 4 to 10, wherein the derivative of aluminium is a salt.
12. A process according to claim 11, wherein the derivative of aluminium is aluminium nitrate or aluminium acetate.
- 15 13. A process according to any of claims 4 to 12, wherein the substance having an archivolt or clathrating effect is a tertiary amine, an amino alcohol, an amino acid, a polyalcohol or a quaternary ammonium base. 15
14. A process according to claim 13, wherein the quaternary ammonium base is a tetraalkylammonium base of the formula  $\text{NR}_4\text{OH}$ , wherein R is an alkyl radical having from 1 to 5 carbon atoms, or a tetraarylammonium base of the formula  $\text{NA}_4\text{OH}$ , wherein A is a phenyl or an alkylphenyl radical. 20
15. A process according to any of claims 4 to 14, wherein the quantity of the substance(s) having an archivolt or clathrating effect is less than the stoichiometric amount with respect to silica or germania. 20
16. A process according to claim 15, wherein the quantity of the substance having an archivolt or clathrating effect is from 0.05 to 0.50 mol per mol of silica or germania. 25
17. A process according to any of claims 4 to 16, wherein the reaction is carried out in the presence of (a) at least one mineralising agent for encouraging crystallisation and/or (b) at least one inorganic base.
18. A process according to claim 17, wherein the or each mineralising agent is a hydroxide or halide of an alkaline earth metal. 30
19. A process according to claim 18, wherein the hydroxide or halide of alkali metal or alkaline earth metal is selected from  $\text{LiOH}$ ,  $\text{NaOH}$ ,  $\text{KOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{KBr}$ ,  $\text{NaBr}$ ,  $\text{NaI}$ ,  $\text{CaI}_2$  and  $\text{CaBr}_2$ .
20. A process according to claim 17, wherein the inorganic base is ammonia or a hydroxide of an alkali metal or an alkaline earth metal.
- 35 21. A process according to claim 20, wherein the hydroxide of the alkali metal or alkaline earth metal is  $\text{NaOH}$ ,  $\text{KOH}$  or  $\text{Ca(OH)}_2$ . 35
22. A process according to any of claims 17 to 21, wherein the quantity of the inorganic base(s) used is less than the stoichiometric amount with respect to silica or germania.
23. A process according to claim 22, wherein the quantity of the inorganic base(s) used is from 0.05 to 0.50 mol per mol of silica or germania. 40
24. A process according to any of claims 4 to 23, wherein a derivative of germanium and/or a derivative of gallium is used, and wherein the crystallisation temperature is from 170 to 210°C.
25. A process according to any of claims 4 to 24, wherein a derivative of germanium and/or a derivative of gallium is used, and wherein an aminoalcohol is used as a crystallisation encouraging agent. 45
26. A process according to claim 4, substantially as described in any of the foregoing Examples.
27. Aluminium-modified or gallium-modified silica or germania, prepared by a process according to any of claims 4 to 26.
28. A process for the alkylation of a hydrocarbon to form a high octane hydrocarbon, wherein the alkylation is carried out in the presence of, as a catalyst, aluminium-modified or gallium-modified silica or germania as claimed in claim 1 or 27 or a zeolite as claimed in claim 2. 50
29. A process according to claim 28, wherein the hydrocarbon contains four carbon atoms.
30. A high octane hydrocarbon obtained by a process according to claim 28 or 29.